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# Sesquiterpenoid Constituents of the Liverwort, *Ptychanthus striatus* (LEHM. et LINDENB.) NEES

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Four sesquiterpenoids, striatene, striatol, β-monocyclonerolidol and ptychanolide, were isolated from the liverwort *Ptychanthus striatus* (LEHM. et LINDENB.)NEES. Their structures have been established by spectroscopic analysis and chemical transformation. Three of them, striatene, striatol and β-monocyclonerolidol, are interesting in terms of the evolution of the liverwort from the algae.

Previously, a number of compounds have been isolated from the liverwort belonging to Jungermanniales.[1] In the course of our investigation on the terpene constituents of the liverwort, we examined the constituents of *Ptychanthus striatus* (LEHM. et LINDENB.) NEES and isolated four new sesquiterpenes, striatene, striatol, β-monocyclonerolidol and ptychanolide together with two known sesquiterpenes, deoxopinguisone[2] and pinguisanene.[3] Three of them, striatene, striatol and β-monocyclonerolidol are interesting in terms of the evolution of the liverwort and the algae. Asakawa *et al.*[3] have reported the identification of mono- and sesquiterpene hydrocarbons, *e.g.* α-pinene, β-pinene, camphene, calamenene, and α-copaene, from the same liverwort. This paper deals in detail with the structural determination of striatene, striatol, β-monocyclonerolidol[4] and ptychanolide.[5]

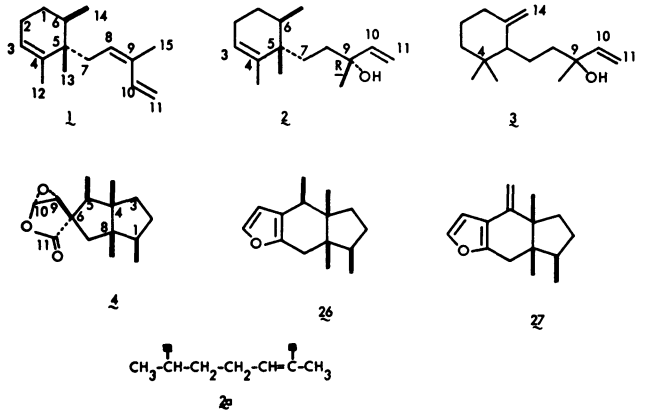


Chart 1.

Striatene (**1**), striatol (**2**), and ptychanolide (**4**) were isolated from the acetone extract of the dry material collected in Tokushima Prefecture in August 1979 by column chromatography on $SiO_2$ using hexane (F-1) and $CHCl_3$ (F-2 and F-3), while striatene (**1**), β-monocyclonerolidol (**3**), and ptychanolide (**4**) were isolated from the dry material collected in Nara Prefecture in November 1979 by similar procedure.

Striatene (**1**), $[\alpha]_D$ +72.7°, was obtained as a colorless oil by preparative GC of the hydrocarbon fraction. The molecular weight by HR-MS together with the $^1H$ and $^{13}C$ NMR data indicated the molecular formula to be $C_{15}H_{24}$. Its IR (1600 $cm^{-1}$) and UV ($\lambda_{max}$ 238 nm, ε 24400) spectra showed the presence of conjugated diene system. The IR (1640 and 990 $cm^{-1}$) and $^1H$ NMR (δ 5.25, 5.28, and 6.91) spectra also showed characteristic bands and signals due to vinyl groups. Moreover, the $^1H$ NMR spectrum showed signals due to a tertiary methyl at δ 0.96, a secondary methyl at δ 0.92, two olefinic methyls at δ 1.69 and 1.88, two trisubstituted double bonds at δ 5.34 and 5.56, and an allylic methylene at δ 2.18 and 2.49.

Striatol (**2**), $[\alpha]_D$ +49.5°, was also obtained as a colorless oil by rechromatography on $AgNO_3$-$SiO_2$ of F-2. The molecular formula $C_{15}H_{26}O$ of **2** was determined by HR-MS together with the $^1H$ and $^{13}C$ NMR data. The IR (3400, 1640, 990, and 880 $cm^{-1}$) spectrum showed bands due to hydroxyl, trisubstituted double bond and vinyl groups. The olefinic functions were further supported by $^1H$ [δ 5.41 (3-H), 5.09, 5.26 (11-$H_{A,B}$), and 5.92 (10-H)], and $^{13}C$ NMR (δ 124.0, 145.1, 139.3, and 111.4) spectra. Moreover, $^1H$ NMR spectrum showed signals due to a secondary methyl at δ 0.87, two tertiary methyls at δ 0.88 and 1.29, and an olefinic methyl at δ 1.59. Treatment of **2** with $POCl_3$ in dry pyridine yielded two trienes, one of which was identified as striatene (**1**) by GLC, IR, and MS. The above spectral data together with this result indicated that striatene and striatol have the same monocyclic carbon skeleton. The presence of the partial structure **2a** was indicated by the results of double irradiation experiments in the $^1H$ NMR spectrum of **2** using $Eu(fod)_3$. Irradiation of the signal of 6-$CH_3$ converted a triplet of quartets of 6-H into a triplet ($J$=6.1 Hz). The fact that 6-H is coupled to 1α- and 1β-H's with $J$=6.1 Hz indicates it is equatorial. Also, irradiation of 1-$H_A$ collapsed the multiplet of 2-$H_A$ to a sharp peak and a triplet of quartets of 6-H to a doublet of quartets. Further, irradiation of the signal due to 2-$H_A$ collapsed a broad singlet due to 3-H and a multiplet due to 1-$H_A$ to sharp peaks.

Striatene (**1**) was oxidized with *m*-chloroperbenzoic acid (MCPBA) in $CH_2Cl_2$ at 0 °C to give two monoepoxides **5** and **6**, the UV spectra of which indicated absorption maximum at 238 nm (ε 19500) due to a conjugated diene. The $^1H$ NMR spectra of epoxides **5** and **6** indicated signals of four olefinic protons (**5**: δ 5.08, 5.21, 5.35, and 6.73; **6**: 5.06, 5.20, 5.67, and 6.82) and a methine proton (**5**: δ 3.01; **6**: 2.77) attached to an epoxy ring. These results indicated that the double

bonds at $C_3/C_4$ was epoxidized. The stereochemistry of oxirane rings in **5** and **6** were determined by $^1H$ NMR using shift reagent, *i.e.*, two protons of $\alpha$-epoxide **6** at C-7 underwent a much larger shift than those of $\beta$-epoxide **5**, thus showing that the oxirane ring and side chain in **6** have a *cis* relation, while those of in **5** have a *trans* relation. The presence of the $C_6$ side chain was suggested by the mass spectra of **1** and **5**, and $^1H$ NMR of **5**. Namely, the mass spectra contained intense ions at *m/z* 123 (M−81) for **1**, *m/z* 139 for **5** and *m/z* 81 for both compounds originating by cleavage of the C-5/C-7 bond. Furthermore, in the $^1H$ NMR spectrum of **5**, irradiation at $\delta$ 5.21 (8-H) collapsed the allylic methylene at $\delta$ 2.15 (7-$H_A$) and 2.41 (7-$H_B$) to AB type doublets and the olefinic methyl protons (9-$CH_3$) at $\delta$=1.86 to a sharp peak. These results indicated that the $C_6$ side chain in **1** is 3-methyl-1,3-pentadiene. In the $^1H$ NMR of **2** with the aid of shift reagents [Eu(fod)$_3$], the proton at C-6 together with the $CH_3$ group at C-4 were observed to have larger shifts than $CH_3$ groups at C-5 and C-6. In the NOE experiments of benzoate **9** (described below), a 2.7% NOE was observed on the 6-$CH_3$ group (axial) upon irradiation of 5-$CH_3$.[6] These results indicated that 6-H and the hydroxyl-containing side chain have a *cis* relation. The geometry of 8-ene in **1** was determined by NOE experiment. An 11% NOE was observed on 8-H upon irradiation of 9-$CH_3$, *i.e.*, the 8-ene is *Z*. These results lead to structures **1** and **2** for striatene and striatol, respectively.

The absolute configurations of **1** and **2** were determined in the following way. Hydrogenation of monoepoxide **5** with Pd/C gave tetrahydro compound **7**, the IR spectrum of which showed the absence of double bond absorption. The $^1H$ NMR spectrum indicated signals of two secondary and one primary methyl groups at $\delta$ 0.74, 0.84, and 0.88. Compound **7** was treated with diethylamine and *n*-BuLi[7] in dry ether to give **8** which was then reacted with *p*-bromobenzoyl chloride in dry pyridine to yield the corresponding monobenzoate **9**. The IR spectrum exhibited bands at 1718, 1640, and 890 $cm^{-1}$ due to an ester group and an exocyclic methylene group. The $^1H$ NMR spectrum indicated the presence of a methine proton adjacent to an oxygen ($\delta$ 5.57), exocyclic methylene protons ($\delta$ 4.76 and 5.08) and protons on an aromatic ring ($\delta$ 7.59 and 7.97). The fact that 3-H is coupled to 2-$H_{A,B}$ with $J$=5.3 and 10.9 Hz indicates that it is axial. The signal of 6-H at $\delta$ 1.67 appeared as a triple quartet, ($J$=4.8 and 6.6 Hz) which collapsed to triplet ($J$=4.8 Hz) on irradiation of 6-$CH_3$. This fact indicates that 6-H is equatorial. In the NOE experiments of **9**, an 11% NOE is observed on 12-$H_A$ upon irradiation of 5-$CH_3$, *i.e.*, 5-$CH_3$ is equatorial. From these results the conformation of this compound was determined to be as shown by **9a**. Harada *et al.* reported that the absolute configuration of cyclic allylic alcohols can be determined nonempirically by the CD exciton chirality method.[8] Application of this method to benzoate **9**, $\Delta\varepsilon_{241}$+3.1, shows that the exocyclic double bond and the 3-OCOPh group constitute a positive chirality as shown in **9b**. Thus, the absolute configuration of striatene is as shown in structure **1**.

The configuration of the *t*-OH group in **2** was determined by taking (*R*)-(−)-linalool (**10**) as the reference sample. Namely, it was found that the *p*-bromobenzoates of striatol and (*R*)-(−)-linalool both show negative Cotton effects at 252 nm (in MeOH), **2b** $\Delta\varepsilon_{252}$−0.4 and **10a** $\Delta\varepsilon_{252}$−0.5. This establishes the C-9 configuration in **2** to be *R*. Recently, Gonnella *et al.*[9] have shown that the benzoate method described above for cyclic compounds is extensible to acyclic secondary allylic alcohols, namely, that the benzoate of acyclic allylic moiety **11** exhibits a positive CD. The present results including that of linalool show that the method is applicable to *t*-OH system **12** as well (because the methyl group is smaller than other alkyl substituents).

$\beta$-Monocyclonerolidol (**3**), $[\alpha]_D$ +3.2°, was obtained as a colorless oil by rechromatography on $AgNO_3$-$SiO_2$

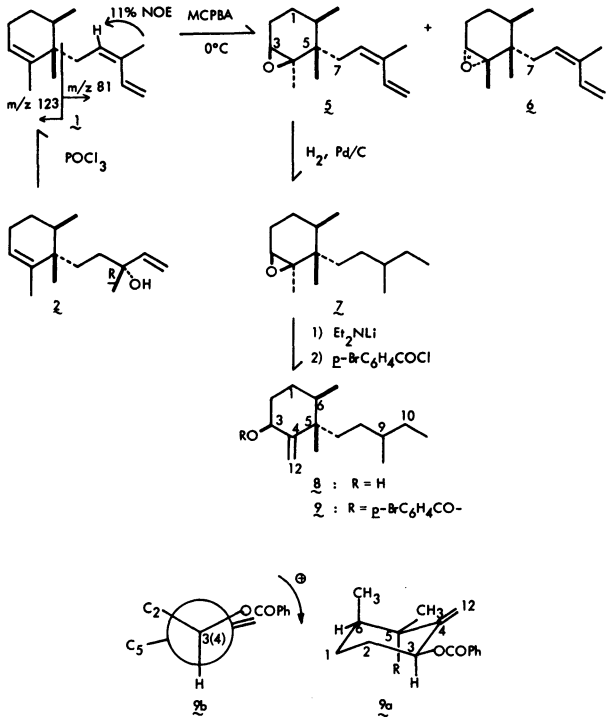



Chart 2.

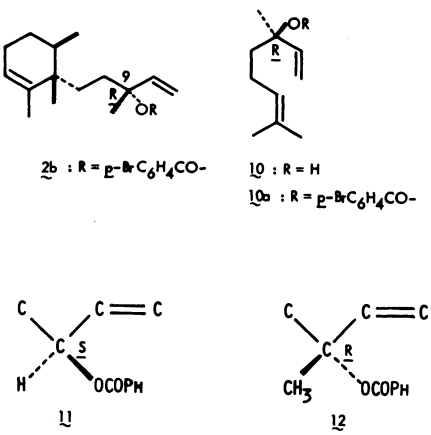



Chart 3.

of F-2′. The molecular formula $C_{15}H_{26}O$ of **3** was determined by HR-MS together with the $^1H$ and $^{13}C$ NMR data. The IR spectrum showed the presence of a hydroxyl group at 3400 $cm^{-1}$, a vinyl group at 1645 and 990 $cm^{-1}$, and an exocyclic methylene group at 890 $cm^{-1}$. The $^1H$ NMR spectrum indicated signals of *gem*-dimethyl groups at $\delta$ 0.84 and 0.92, a tertiary methyl group on a carbon bearing hydroxyl at $\delta$ 1.27, an exocyclic methylene group at $\delta$ 4.53 and 4.75, and vinyl groups at $\delta$ 5.02, 5.18, and 5.91. The mass spectrum indicated intense ion peaks at *m/z* 123 (M−18−81) and *m/z* 81 as observed in **1** and **2**. The fact indicates that **3** also has a $C_6$ side chain. From these results together with biogenetic consideration, we assumed that **3** had a monocyclonerolidol skeleton as shown by structure **3**. This assumption was confirmed by partial synthesis of **3** from α-ionone.

Hydrogenation of commercial (±)-α-ionone **13** with Pd/C in 1.5% KOH-EtOH gave the hydrogenated mixture, from which dihydroionone **14** was separated by column chromatography on $SiO_2$. Dihydroionone **14** exhibited the molecular ion peak at *m/z* 194 in its mass spectrum. The IR spectrum exhibited bands at 1710 and 810 $cm^{-1}$ due to a carbonyl group and a trisubstituted double bond. The $^1H$ NMR spectrum indicated the presence of an olefinic methyl group ($\delta$ 1.66) and a trisubstituted double bond ($\delta$ 5.31). The reaction of **14** with ethylene glycol and TsOH yielded acetal **15**, the $^1H$ NMR spectrum of which exhibited a signal due to the acetal group at $\delta$ 3.90. The IR spectrum showed the absence of a carbonyl group. Next, irradiation of acetal **15** in ether containing 10% phenol with a 450 W-Hg lamp[10] afforded a mixture of **16** and starting material **15**. Then, this mixture was hydrolyzed with TsOH in THF containing $H_2O$ to give a ketone mixture, **16a** and **14**, from which the exocyclic isomer **16a** was separated by column chromatography on $AgNO_3$-$SiO_2$. The IR spectrum showed exocyclic methylene absorption bands at 1640 and 885 $cm^{-1}$, and a carbonyl absorption band at 1710 $cm^{-1}$. The $^1H$ NMR spectrum also suggested the presence of an exocyclic methylene group at $\delta$ 4.49 and 4.74. The exocyclic isomer **16a** was reacted with vinylmagnesium bromide (prepared from vinyl bromide and magnesium in THF) in dry THF to give the racemic alcohol **17**. The NMR, IR, and mass spectra of **17** were identical with those of β-monocyclonerolidol (**3**).

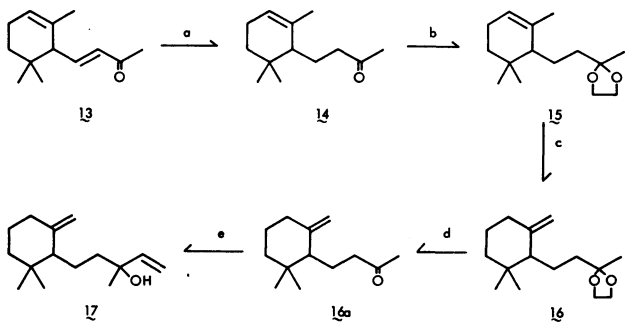



Chart 4.

a) $H_2$, pd/C, 1.5% KOH-EtOH; b) Ethylene glycol, TsOH c) 10% Penol/ether, $h\nu$(450 W); d) TsOH, THF THF; e) $CH_2$=CHMgBr, THF.

On the basis of distribution of terpenoids, Asakawa and co-workers[11] have noted that liverwort are closely related to algae. The fact that the skeletal structures of **1**—**3** are identical with α- and β-snyderol,[12] microcionin,[13] *etc.*[14] which have been found in marine algae and in marine animals feeding on algae, supports the notion that liverworts have evolved from algae.

Ptychanolide (**4**), mp 143—144 °C, $[\alpha]_D$ +23.2° was obtained as a colorless needles by recrystallization of F-2 and 2′. The molecular formula $C_{15}H_{22}O_3$ of **4** was determined by the appearance of a molecular ion peak at 250.1565 in the HR-MS. The IR spectrum showed the presence of a γ-lactone absorption band at 1780 $cm^{-1}$ and the absence of hydroxyl absorptions. The $^1H$ NMR spectrum indicated signals due to two secondary $CH_3$ groups at $\delta$ 0.84 and 0.98, two tertiary $CH_3$ groups at $\delta$ 0.79 and 0.93, an isolated methylene group at $\delta$ 1.39 and 1.99, and two methine protons adjacent to oxygen at $\delta$ 3.55 and 5.52. The $^{13}C$ NMR spectrum also suggested the presence of a γ-lactone group at $\delta$ 76.1 and 179.8. Hence the remaining oxygen atom was attributed to an ether linkage. Treatment of the lactone **4** with 10% $H_2SO_4$ in acetone afforded the diol lactone **18**. The IR spectrum showed bands at 3500 and 1770 $cm^{-1}$ due to hydroxyl and γ-lactone groups. The $^1H$ NMR spectrum indicated signals of two methine protons adjacent to oxygen at $\delta$ 4.13 and 5.62 which were coupled with each other. The formation of an α-glycol from an ether indicates that the diol is derived from an epoxide. The lactone **4** was reduced with LAH in dry ether to triol **19**, the $^1H$ NMR spectrum of which showed signals of five protons adjacent to oxygen at $\delta$ 3.64, 3.72, 3.76, 3.84, and 3.92. In decoupling experiments, irradiation at $\delta$ 3.92 collapsed the two double doublets of the $-C\underline{H}_2OH$ group at $\delta$ 3.72 and 3.76 to AB type doublets. This result and assignments of *J* values suggested that a hydroxymethyl group at C-11 and 1,2-diol system at C-9 and C-10 are attached to a quaternary carbon. Hence, the γ-lactone must form a spiro linkage at C-6 and the epoxy ring is attached to the γ-lactone ring.

Oxidation of triol **19** with $NaIO_4$ gave aldehyde **20**, $M^+$ *m/z* 224 ($C_{14}H_{24}O_2$), the IR spectrum of which showed bands at 3560, 3450, and 1715 $cm^{-1}$ due to hydroxyl and formyl group. The $^1H$ NMR spectrum indicated signals of two protons adjacent to an oxygen as primary alcohol at $\delta$ 3.55 and 3.94, and proton of formyl group at $\delta$ 9.69 instead of three protons adjacent to oxygen in **19**. Aldehyde **20** was further oxidized with MCPBA in $CH_2Cl_2$, followed by hydrolysis with $Al_2O_3$ to yield diol **21** ($M^+$, *m/z* 212; $C_{13}H_{24}O_2$). Its IR spectrum showed the presence of a hydroxyl absorption band at 3325 $cm^{-1}$ and the absence of carbonyl absorption. The diol **21** was oxidized further with $NaIO_4$ to the corresponding ketone **22** which exhibited a molecular ion peak at 180 ($C_{12}H_{20}O$) in the mass spectrum. The IR spectrum indicated the presence of a five-membered ring ketone (1740 $cm^{-1}$). These results establish that ptychanolide **4** has a spiro lactone moiety at C-6. Reduction of ketone **22** with LAH in dry ether afforded alcohols **23** and **24**, the $^1H$ NMR

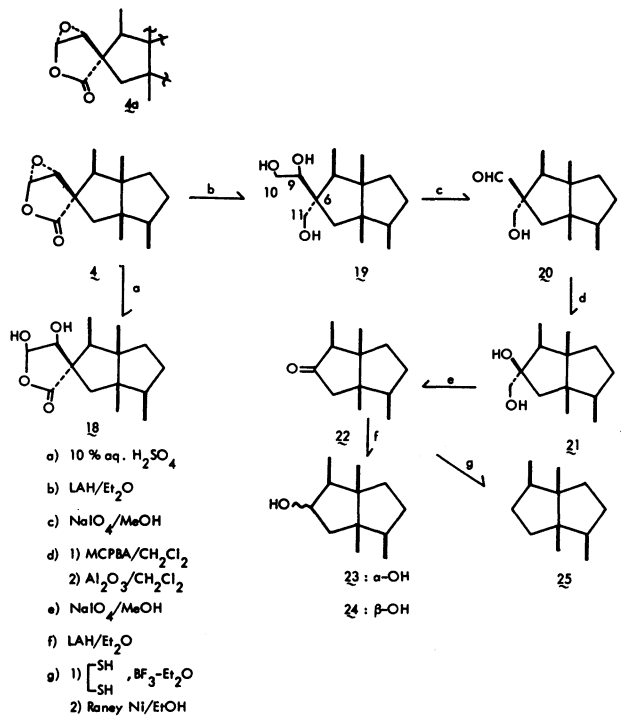



Chart 5.

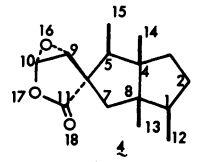
spectra of which showed signals of protons on carbons bearing hydroxyl groups (**23**: $\delta$ 3.77; **24**: 4.20), respectively. In the decoupling experiments of **23**, irradiation of 6-H as a double triplet collapsed a pair of double doublets of 7-$CH_2$ at $\delta$ 1.49 and 1.79 to a pair of doublets and a double quartet of 5-H at $\delta$ 1.74 to a quartet. This fact indicated that the OH function was flanked by a methylene group and secondary $CH_3$ group. Namely, ptychanolide has a partial structure **4a**. Ketone **22** was treated with 1,2-ethanedithiol to give the corresponding thioacetal which was desulfurized with Raney Ni in EtOH to yield the volatile hydrocarbon **25**. Its mass spectrum showed a molecular ion peak at 166 ($C_{12}H_{22}$). However, the $^1H$ and $^{13}C$ NMR spectra showed only the signals of two methyl groups and five protons, and those of six carbons, respectively. Therefore, the hydrocarbon **25** has the symmetric bicyclo[3.3.0]octane skeleton. The above results indicate that ptychanolide is represented by formula **4** (planar).

The stereostructure of ptychanolide (**4**) was determined by X-ray analysis. The colorless transparent crystals of **4**, which were recrystallized from hexane-EtOAc, belong to orthorhombic with space group $p2_12_12_1$. The crystal data are as follows: $C_{15}H_{22}O_3$, $M_r$= 250.16, $a$=6.514(1), $b$=19.376(4), $c$=10.543(3) Å, $v$= 1330.7(5) Å$^3$, $Z$=4, $D_m$=1.233 (1), $D_x$=1.249 g cm$^{-3}$. X-Ray diffraction intensities were measured by Rigaku automatic diffractometer with graphite-monochromated Cu $K\alpha$ radiation using a $\theta$-2$\theta$ scan mode and a scan rate of 4°/min. Stationary background counts (5 s each) were taken at both limits of each scan (scan width in 2$\theta$: 1.2+0.15 tan$\theta$). A total of 1344 unique reflections were measured to the limit 2$\theta$=130°. Lorentz and polarization corrections were applied, but no absorption correction was made because of the small size of the used crystal (dimension: 0.3×0.4×0.2 mm$^3$). The X-ray intensities of four standard reflections monitored at 100 reflection intervals showed no evidence of structural deterioration during the data collection.

The structure was solved by the direct methods with program MULTAN78.[15] An E-map, calculated using 200 reflections ($|E|>1.40$) with the phase set of the highest combined figure of merit (=2.86), revealed the positions of all nonhydrogen atoms. These coordinates were refined by a full-matrix least-squares method with isotropic temperature factors and then by a block-diagonal least-squares method with anisotropic ones. All hydrogen atoms could be located from a difference Fourier map and these were included in a further refinement with isotropic temperature factors. The final $R$ value was 0.078. The final positional parameters with their estimated standard deviations of nonhydrogen atoms are listed in Table 1.

Table 1. Atomic coordinates (× $10^4$) of nonhydrogen atoms of **4**

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| C1 | 4160 (11) | 977 (3) | 5420 (6) |
| C2 | 3997 (11) | 237 (3) | 5870 (8) |
| C3 | 5405 (11) | 162 (4) | 7049 (8) |
| C4 | 6291 (8) | 886 (3) | 7297 (6) |
| C5 | 4842 (9) | 1322 (3) | 8111 (6) |
| C6 | 5179 (8) | 2073 (3) | 7648 (6) |
| C7 | 6138 (9) | 2006 (3) | 6283 (6) |
| C8 | 6217 (8) | 1238 (3) | 5977 (5) |
| C9 | 6445 (9) | 2549 (3) | 8451 (6) |
| C10 | 5357 (11) | 3181 (4) | 8584 (6) |
| C11 | 3183 (9) | 2479 (3) | 7560 (6) |
| C12 | 3899 (12) | 1056 (4) | 3983 (8) |
| C13 | 8035 (10) | 1071 (4) | 5107 (7) |
| C14 | 8450 (10) | 842 (4) | 7867 (7) |
| C15 | 4977 (12) | 1232 (4) | 9551 (7) |
| O16 | 5529 (7) | 2767 (3) | 9630 (4) |
| O17 | 3428 (7) | 3132 (2) | 7980 (5) |
| O18 | 1566 (6) | 2293 (2) | 7122 (5) |



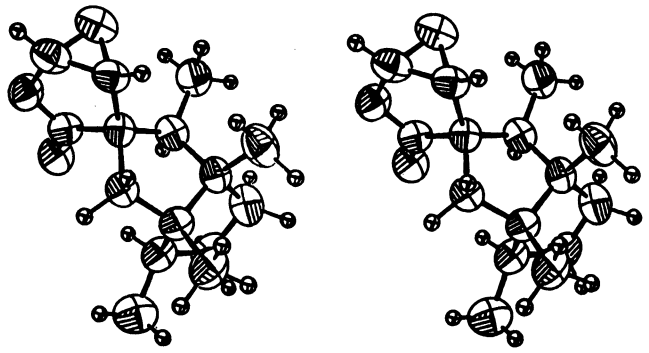


Fig. 1. Perspective drawing of ptychanolide **4**.

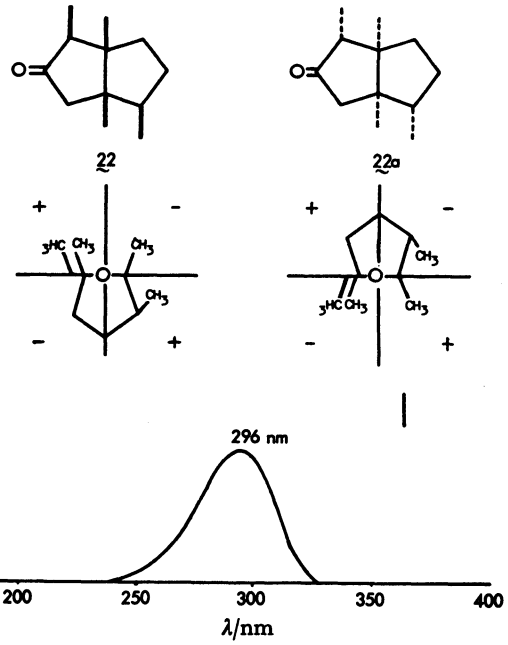



Fig. 2. CD spectrum of **22**.

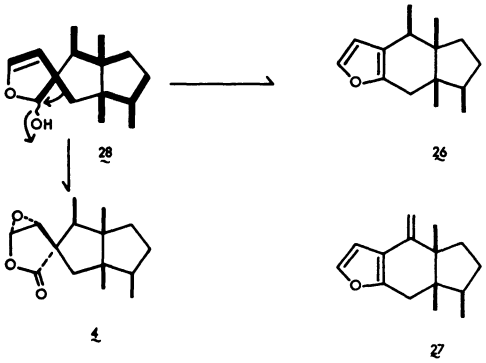


Chart 6.

The atomic scattering factors for all atoms were taken from "International Tables for X-Ray Crystallography."[16] All numerical calculations were carried out on an ACOS-700 computer at the Computation Center of Osaka University using *UNICS* program.[17] The stereostructure of **4** is shown in Fig. 1. The relative stereostructure of ptychanolide (**4**) was thus clarified. Furthermore, the keto compound **22** showed a positive Cotton effect at 295 nm in the CD spectrum (Fig. 2). The positive sign of the Cotton effect can be understood by application of the octant rule[18] to the cyclopentanone system, as visualized in octant projection formula **22** and **22a**. This leads to the absolute configuration shown for **22** which is corroborated by the established configuration of congeners **26**[2,19] and **27**.[3] Thus, the absolute structure of ptychanolide is shown by formula **4**.

The biogenesis of the pinguisone type sesquiterpenoids represented by deoxopinguisone **26** and pinguisanene **27** is as yet not clear. However, the isolation of ptychanolide **4** from the same liverwort suggests that they are derived from an intermediate such as **28**.

## Experimental

All melting points are uncorrected. IR spectra were measured with a Hitachi EPI-G2 spectrometer, $^{13}C$ NMR spectra with a JEOL FX-100 (25.0 MHz) spectrometer, $^1H$ NMR spectra with a JEOL FX-100 (100 MHz), a Nicolet NT-360 (360 MHz) or a Hitachi R-20B (60 MHz) spectrometer in deuteriochloroform solution containing tetramethylsilane as an internal standard, low resolution mass spectra with a Hitachi RMU-6 mass spectrometer and high resolution mass spectra with a JEOL 01SG-2, with direct inlet system operating at 70 eV. CD spectra were measured with a JASCO J-20 spectrometer. An analytical GC was performed with a Hitachi 163-type apparatus equipped with a Thermon 600T glass capillary column, and preparative GC with Varians model 90 fitted OV-17 on Chromosorb-W, operated at 150°. Kieselgel 60 (E. Merck, Darmstadt) and Silica CC-7 special (Mallinckrodt) were used for column chromatography. Thin-layer chromatography (TLC) was carried out on Kieselgel $GF_{254}$ (E. Merck, Darmstadt) in 0.25 mm thickness.

*Extraction and Isolation.* The dry material (100 g) of *Ptychanthus striatus* (Lehm. et Lindenb.) Nees collected in Wakayama Prefecture around Kosa-cho in March 1980 was extracted with acetone at room temperature. Acetone was evaporated under vacuum and the concentrate was extracted with $CHCl_3$. The $CHCl_3$ extract (6.6 g) was subjected to column chromatography over $SiO_2$. The fraction eluted with hexane gave sesquiterpene hydrocarbons (F-1) containing striatene (**1**), deoxopinguisone (**26**), and pinguisanene (**27**). The fraction eluted with $CHCl_3$ yielded crude ptychanolide (**4**) (F-2) and crude striatol (**2**) (F-3). Also, F-1′, F-2′, and F-3′ were isolated from the acetone extract of the dry material (100 g) collected in Nara Prefecture around Ikadaba in November 1979 by a similar procedure.

Striatene (**1**) was isolated from hydrocarbon fractions, F-1 and F-1′, by preparative GC, as a colorless oil (**1**, 200 mg from F-1 and F-1′, respectively), $[\alpha]_D^{22}$ +72.7° (*c* 1.19, $CHCl_3$), IR (film) 1640, 1600, 990, 810 $cm^{-1}$; UV (cyclohexane) 232 (sh), 238 (ε 24400) and 245 (sh) nm; $^1H$ NMR δ 0.92 (3H, d, $J$=6.5 Hz, 6-$CH_3$), 0.96 (3H, s, 5-$CH_3$), 1.69 (3H, br.s, 4-$CH_3$), 1.88 (3H, br.s, 9-$CH_3$), 2.18 (1H, dd, $J$=6.0, 16.0 Hz, 7-$H_A$), 2.49 (1H, dd, $J$=8.0, 16.0 Hz, 7-$H_B$), 5.25 (1H, dd, $J$=1.6, 10.5 Hz, 11-$H_A$), 5.28 (1H, dd, $J$=1.6, 17.3 Hz, 11-$H_B$), 5.34 (1H, m, 8-H), 5.56 (1H, t-like, 3-H), and 6.91 (1H, dd, $J$=10.5, 17.3 Hz, 10-H); $^{13}C$ NMR δ 16.0 (q), 19.2 (q), 20.0 (q), 20.7 (q), 25.3 (t), 27.1 (t), 34.2 (t), 34.2 (d), 40.7 (s), 113.2 (t), 124.4 (d), 128.1 (d), 134.0 (d), 133.2 (s), and 139.1 (s); MS *m/z* (%) 204 (7, $M^+$), 123 [100, $(M-81)^+$] and 81 (25). Found: *m/z* 204.1866. Calcd for $C_{15}H_{24}$: M, 204.1856.

*Epoxidation of Striatene (1).* The solution of *m*-chloroperbenzoic acid (390 mg) in $CH_2Cl_2$ (5 ml) was added to an ice-cooled solution of **1** (300 mg) in $CH_2Cl_2$ (5 ml) and the mixture was stirred for 40 min at 0 °C. The reaction mixture was treated in the usual way to give residue (190 mg), which was chromatographed on 10% $AgNO_3$–$SiO_2$ (Mallinckrodt, CC-7). Elution with $CH_2Cl_2$–EtOAc (20 : 1) gave β-epoxide **5** (55 mg) as a colorless oil. Successive elution with the same solvent gave α-epoxide **6** (10 mg) as a colorless oil.

*β-Epoxide 5*: IR (film) 1640, 1600, 980, 900 $cm^{-1}$; UV (cyclohexane) 237 nm (ε 19500); $^1H$ NMR δ 0.75 (3H, d, $J$=6.5 Hz, 6-$CH_3$), 0.92 (3H, s, 5-$CH_3$), 1.26 (3H, s, 4-$CH_3$), 1.86 (3H, br.s, 9-$CH_3$), 2.15 (1H, dd, $J$=5.5, 17.0 Hz, 7-$H_A$), 2.41 (1H, dd, $J$=7.5, 17.0 Hz, 7-$H_B$), 3.01 (1H, br.s, 3-H), 5.08 (1H, dd, $J$=1.5, 10.5 Hz, 11-$H_A$), 5.21 (1H, t-like, 8-H), 5.35 (1H, dd, $J$=1.5, 17.5 Hz, 11-$H_B$), and 6.73 (1H, dd, $J$=10.5, 17.5 Hz, 10-H); MS *m/z* (%) 220 (3, $M^+$, $C_{15}H_{24}O$), 205 [8, $(M-CH_3)^+$], 139 [98, $(M-81)^+$], 109 (92), 95 (100), 81 (99), 43 (98).

*α-Epoxide 6*: IR (film) 1645, 1605, 980, 900 $cm^{-1}$; UV

(cyclohexane) 238 nm (ε 18000); $^1$H NMR δ 0.72 (3H, d, $J$=6.5 Hz, 6-$CH_3$), 0.91 (3H, s, 5-$CH_3$), 1.27 (3H, s, 4-$CH_3$), 1.86 (3H, br.s, 9-$CH_3$), 2.36 (2H, br.s, 7-$H_{A,B}$), 2.77 (1H, t, $J$=1.5 Hz, 3-H), 5.06 (1H, dd, $J$=1.5, 10.5 Hz, 11-$H_A$), 5.20 (1H, dd, $J$=1.5, 17.5 Hz, 11-$H_B$), 5.67 (1H, br.t, $J$=4.0 Hz, 8-H), and 6.82 (1H, dd, $J$=10.5, 17.5 Hz, 10-H); MS $m/z$ (%) 220 (trace, $M^+$, $C_{15}H_{24}O$), 139 [17, $(M-81)^+$], 95 (30), 81 (20), 43 (100).

*Hydrogenation of β-Epoxide 5.* β-Epoxide **5** (10 mg) and 10% palladium charcoal (10 mg) in EtOH (1 ml) were stirred under hydrogen atmosphere at room temperature for 5 h. The catalyst was removed by filtration and the solvent was evaporated to give a residue (11 mg), which was chromatographed on $SiO_2$. Elution with $CHCl_3$ yielded tetrahydro epoxide **7** (7 mg), colorless oil, $^1$H NMR δ 0.74 (3H, d, $J$=6.5 Hz, $s$-$CH_3$), 0.84 (3H, d, $J$=7.5 Hz, $s$-$CH_3$), 0.86 (3H, s, 5-$CH_3$), 0.88 (3H, t, $J$=6.6 Hz, 10-$CH_3$), 1.24 (3H, s, 4-$CH_3$), and 2.96 (1H, br.s, 3-H); MS $m/z$ (%) 224 (12, $M^+$, $C_{15}H_{28}O$), 209 [31, $(M-CH_3)^+$], 103 (100), 85 (98), 43 (76).

*Conversion of 7 into Benzoate 9.* Commercial butyllithium (0.3 ml, 15% solution in hexane) was added to a solution of diethylamine (36.5 mg) in dry ether (1 ml). Tetrahydro epoxide **7** (18 mg) in dry ether (1 ml) was then added and the mixture was refluxed for 3 h. The reaction mixture was poured into NaCl aqueous solution and extracted with ether. The ether layer was treated in the usual way to give residue (14 mg), which was treated with $p$-bromobenzoyl chloride (20 mg) in dry pyridine (2 ml) at room temperature for a day. The reaction mixture was treated in the usual way to give a residue, which was chromatographed on $SiO_2$. Elution with hexane–EtOAc (20 : 1) gave benzoate **9** (8 mg), colorless viscous oil, IR (film) 1718, 1640, 890 cm$^{-1}$; UV (MeOH) 205.5, 244 nm (ε 16900, 17500); CD, $\Delta\varepsilon_{241}$ +3.06 ($c$ 0.145, MeOH); $^1$H NMR δ 0.82 (3H, t, $J$=6.6 Hz, 10-$CH_3$), 0.83 (3H, d, $J$=6.6 Hz, 9-$CH_3$), 0.90 (3H, d, $J$=6.7 Hz, 6-$CH_3$), 1.01 (3H, s, 5-$CH_3$), 1.67 (1H, tq, $J$=4.8, 6.6 Hz, 6-H), 4.76 (1H, br.s, 12-$H_A$), 5.08 (1H, br.s, 12-$H_B$), 5.57 (1H, dd, $J$=5.3, 10.9 Hz, 3-H), 7.59 (2H, aromatic protons) and 7.98 (2H, aromatic protons); MS $m/z$ (%) 408, 406 (trace, $M^+$, $C_{22}H_{31}O_2Br$), 323, 321 [45, 47, $(M-85)^+$], 185, 183 [92, 91, ($p$-$BrC_6H_4CO)^+$], 122 (100), 93 (69).

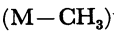
*Benzoylation of (R)-(−)-Linalool (10).* The mixture of (*R*)-(−)-linalool (**10**) (20 mg) isolated from Ho leaf oil and $p$-bromobenzoyl chloride (20 mg) in dry pyridine (1 ml) was kept at room temperature for 2 d. The reaction mixture was treated in the usual way to yield a residue, which was chromatographed on $SiO_2$. Elution with $CHCl_3$ gave a benzoate **10a** (15 mg), colorless oil, IR (film) 1720, 1645, 910, 830 cm$^{-1}$; UV (EtOH) 206.5, 244.5 nm (ε 14500, 16400); CD, $\Delta\varepsilon_{252}$ −0.54 ($c$ 2.5, EtOH); $^1$H NMR δ 1.57, 1.62 (3H each, br.s), 1.68 (3H, s, 6-$CH_3$), 1.76—2.28 (4H, 4-$H_{A,B}$, 5-$H_{A,B}$), 5.12 (1H, m, 3-H), 5.17 (1H, dd, $J$=1.2, 10.0 Hz, 8-$H_A$), 5.23 (1H, dd, $J$=1.2, 17.5 Hz, 8-$H_B$), 6.07 (1H, dd, $J$=10.0, 17.5 Hz, 7-H), 7.52 (2H, aromatic protons) and 7.85 (2H, aromatic protons); MS $m/z$ (%) 185, 183 [100, 98 ($p$-$BrC_6H_4)^+$], 136 (43).

*Isolation of Striatol (2).* Fraction 3 (F-3) was rechromatographed on 10% $AgNO_3$–$SiO_2$ eluted with hexane–EtOAc (10 : 1) to yield colorless viscous oil (**2**, 70 mg), $[\alpha]_D^{22}$ +49.5° ($c$ 1.2, $CHCl_3$); IR (film) 3400, 1640, 990, 800 cm$^{-1}$; $^1$H NMR δ 0.87 (3H, d, $J$=6.5 Hz, 6-$CH_3$), 0.88 (3H, s, 5-$CH_3$), 1.29 (3H, s, 9-$CH_3$), 1.59 (3H, br.s, 4-$CH_3$), 5.09 (1H, dd, $J$=1.6, 10.5 Hz, 11-$H_A$), 5.26 (1H, dd, $J$=1.6, 17.5 Hz, 11-$H_B$), 5.41 (1H, m, 3-H) and 5.92 (1H, dd, $J$=10.5, 17.5 Hz, 10-H); $^{13}$C NMR δ 15.7 (q), 19.0 (q), 21.0 (q), 27.6 (q), 25.4 (t), 27.0 (t), 30.1 (t), 36.5 (t), 33.2 (d), 40.0 (s), 73.1 (s), 111.4 (t), 124.0 (d), 145.1 (d), 139.3 (s); MS $m/z$ (%) 204 [17, $(M-18)^+$], 123 [100, $(M-81)^+$], 81 (44). Found: $m/z$ 222.1994, Calcd for $C_{15}H_{26}O$: M, 222.2004.

*Benzoylation of Striatol (2).* A solution of striatol **2** (10 mg) and $p$-bromobenzoyl chloride (10 mg) in dry pyridine (1 ml) was kept at room temperature for 2 d. The reaction mixture was treated in the usual way to give a residue, which was purified by $SiO_2$ column chromatography using hexane–EtOAc (15 : 1) to afford benzoate **2b** (7 mg), colorless viscous oil, IR (film) 1720, 1645, 980, 800 cm$^{-1}$; UV (EtOH) 206, 244.5 nm (ε 16000, 18000); CD, $\Delta\varepsilon_{252}$ −0.4 ($c$ 2.7, EtOH), $^1$H NMR δ 0.81 (3H, d, $J$=7.0 Hz, 6-$CH_3$), 0.81 (3H, s, 5-$CH_3$), 1.59 (3H, br.s, 4-$CH_3$), 1.69 (3H, s, 9-$CH_3$), 5.17 (1H, dd, $J$=1.6, 10.5 Hz, 11-$H_A$), 5.22 (1H, dd, $J$=1.6, 17.5 Hz, 11-$H_B$), 5.40 (1H, m, 3-H), 6.03 (1H, dd, $J$=10.5, 17.5 Hz, 10-H), 7.53 (2H, aromatic protons) and 7.85 (2H, aromatic protons); MS $m/z$ (%) 185, 183 [100, 98 ($p$-$BrC_6H_4CO)^+$], 204 (20), 123 (95), 81 (30).

*Isolation of β-Monocyclonerolidol (3).* Fraction 3′ (F-3′) was purified by column chromatography on 10% $AgNO_3$–$SiO_2$ using hexane–EtOAc (10 : 1) to give β-monocyclonerolidol (**3**, 70 mg), colorless viscous oil, $[\alpha]_D^{25}$ +3.2° ($c$ 0.66, $CHCl_3$); IR (film) 3400, 1645, 990, 890 cm$^{-1}$; $^1$H NMR δ 0.84, 0.92 (3H each, s, *gem*-dimethyl at C-4), 1.27 (3H, s, 9-$CH_3$), 4.53 (1H, br.s, 14-$H_A$), 4.75 (1H, br.s, 14-$H_B$), 5.02 (1H, dd, $J$=1.6, 10.5 Hz, 11-$H_A$), 5.18 (1H, dd, $J$=1.6, 17.5 Hz, 11−$H_B$), and 5.91 (1H, dd, $J$=10.5, 17.5 Hz, 10H); $^{13}$C NMR δ 20.4 (q), 26.4 (q), 27.7 (q), 23.7 (t), 28.5 (t), 32.4 (t), 36.2 (t), 41.1 (t), 54.5 (d), 35.0 (s), 73.3 (s), 109.0 (t), 111.4 (t), 145.4 (d), 149.3 (s); MS $m/z$ (%) 204 [25, $(M-H_2O)^+$], 189 (40), 123 [100, $(M-18-81)^+$], 109 (43), 93 (43), 81 (75). Found: $m/z$ 222.1992. Calcd for $C_{15}H_{26}O$: M, 222.2004.

*Hydrogenation of α-Ionone (13).* The mixture of α-ionone **13** (500 mg) and Pd/C (50 mg) in EtOH containing 1.5% KOH was stirred under hydrogen atmosphere at room temperature for 4 h. The reaction mixture was filtered and the filtrate was neutralized with 5% aqueous HCl, diluted with $H_2O$, and extracted with ether. The ether layer was treated in the usual way to give a residue, which was chromatographed on $SiO_2$. Elution with $CHCl_3$ yielded dihydroionone **14** (190 mg), colorless oil, IR (film) 1710, 810 cm$^{-1}$; $^1$H NMR δ 0.88, 0.93 (3H each, s, *gem*-dimethyl), 1.66 (3H, br.s, $=C(CH_3)$), 2.12 (3H, s, $COCH_3$), 5.31 (1H, m, $=CH$); MS $m/z$ (%) 194 (4, $M^+$, $C_{13}H_{22}O$), 176 [23, $(M-CH_3)^+$], 161 [17, $(M-30)^+$], 136 [80, $(M-15-43)^+$], 121 (100), 43 (84).

*Acetalization of Dihydroionone 14.* A solution of dihydroionone **14** (500 mg) in benzene (40 ml) containing ethylene glycol (6 ml) and TsOH (0.13 g) was stirred at reflux with a Dean-Stark trap for 12 h. The reaction mixture was washed with aqueous $NaHCO_3$ and $H_2O$, and dried over $Na_2SO_4$. The solvent was removed *in vacuo* to give a residue (580 mg), which was chromatographed on $SiO_2$. Elution with $CHCl_3$ gave acetal **15** (400 mg), colorless oil, IR (film) 1650, 1060, 860 cm$^{-1}$; $^1$H NMR δ 0.86, 0.92 (3H each, s, *gem*-dimethyl) 1.30 (3H, s,  ), 1.66 (3H, br. s, $=C(CH_3)$), 3.90 (4H, s), 5.27 (1H, br.s, $HC=$); MS $m/z$ (%) 238 (1, $M^+$, $C_{15}H_{26}O_2$), 223 [2, $(M-CH_3)^+$], 136 (25), 87 [100,  ], 43 (19).

*Irradiation of Acetal 15.* A solution of acetal **15** (2 g) in ether (270 ml) containing phenol (30 g) was irradiated with 450 W-Hg lamp for 3 h. The reaction mixture was passed an $Al_2O_3$ column by elution with ether. The ether fraction was evaporated under vacuum to give a residue (1.5 g), which was chromatographed on 10% $AgNO_3$–$SiO_2$ to yield β-isomer **16** (550 mg) and starting material **15** (600 mg). β-Isomer **16**,

colorless oil, IR (film) 1640, 1070, 890 $cm^{-1}$; $^1H$ NMR $\delta$= 0.84, 0.94 (3H each, s, *gem*-dimethyl), 1.31 (3H, s, $\ulcorner O \urcorner O$-$CH_3$), 3.92 (4H, s), 4.52, 4.73 (1H each, br.s, $=\langle^H_H$); MS *m/z* (%) 238 (58, $M^+$, $C_{15}H_{26}O_2$), 223 [100, $(M-CH_3)^+$], 178 (73), 176 (93), 161 (97), 136 (98), 87 [99, $(CH_3\langle^O_O\rangle)^+$]. 43 (70).

*Hydrolysis of Acetal* **16**. The mixture of acetal **16** (300 mg) and TsOH (20 mg) in THF (10 ml) and $H_2O$ (1 drop) was kept at room temperature for 2 d. The reaction mixture was diluted with $H_2O$ and extracted with $CH_2Cl_2$. The $CH_2Cl_2$ layer was treated in the usual way to afford a residue (250 mg), which was purified by $SiO_2$ column chromatography using $CH_2Cl_2$ to yield ketone **16a** (190 mg), colorless oil, IR (film) 1710, 1640, 885 $cm^{-1}$; $^1H$ NMR $\delta$ 0.94, 0.96 (3H each, s, *gem*-dimethyl), 2.00 (3H, s, $-COCH_3$), 4.49, 4.74 (1H each, br. s, $=\langle^H_H$); MS *m/z* (%) 194 (2, $M^+$, $C_{13}H_{22}O$), 176 [25, $(M-CH_3)^+$], 161 (27), 136 (59), 121 (68), 43 (100).

*Grignard Reaction of Ketone* **16a**. After a solution of ketone **16a** (250 mg) in dry THF (5 ml) was added dropwise to a stirred solution of vinylmagnesium bromide (prepared from 3 g of vinyl bromide and 720 mg of Mg in 10 ml of dry THF) at room temperature, the mixture was heated under reflux for 3 h. The reaction mixture was then decomposed by addition of a saturated solution of $NH_4Cl$. The water layer was extracted with ether and the ether extract dried over $Na_2SO_4$. The solvent was evaporated under vacuum to give a residue, which was chromatographed on $SiO_2$. Elution with $CHCl_3$ yielded alcohol **17** (123 mg).

The IR, NMR, and mass spectra were found to be identical with those of $\beta$-monocyclonerolidol (**3**).

*Isolation of Ptychanolide* (**4**). The crude ptychanolide (F-2 and F-2′) was recrystallized with hexane–EtOAc to yield colorless needles (**4**, 270 mg, 120 mg), mp 143—144 °C, $[\alpha]_D^{24}$ +23.2° (*c* 0.47, $CHCl_3$); IR (KBr) 1780 $cm^{-1}$; $^1H$ NMR $\delta$ 0.79, 0.93 (3H each, s, 4-$CH_3$, 8-$CH_3$), 0.84 (3H, d, $J$=7.7 Hz, 1-$CH_3$), 0.98 (3H, d, $J$=7.7 Hz, 5-$CH_3$), 1.3—1.4 (2H, m, 2-$H_A$, 3-$H_A$), 1.39 (1H, d, $J$=13.6 Hz, 7-$H_A$), 1.71 (1H, m, 2-$H_B$), 1.87 (1H, m, 3-$H_B$), 1.99 (1H, d, $J$=13.6 Hz, 7-$H_B$), 2.38 (1H, m, 1-H), 2.61 (1H, q, $J$=7.7 Hz), 3.55 (1H, d, $J$= 2.4 Hz, 9-H and 5.52 (1H, d, $J$=2.4 Hz, 10-H); $^{13}C$ NMR $\delta$ 10.7 (q), 14.5 (q), 16.7 (q), 18.4 (q), 31.0 (t), 35.5 (t), 44.6 (t), 42.0 (d), 50.0 (d), 54.4 (s), 55.3 (s), 56.3 (s), 57.5 (d), 76.1 (d), 179.8 (s); MS *m/z* (%) 250 (6, $M^+$), 235 [13, $(M-CH_3)^+$], 205 (24), 109 (100). Found: *m/z* 250.1565. Calcd for $C_{15}H_{22}O_3$: M, 250.1564.

*Hydrolysis of Ptychanolide* (**4**). After 10% aqueous $H_2SO_4$ was added to a solution of ptychanolide **4** (20 mg) in acetone (2 ml) at 0 °C, the mixture was kept at room temperature for 3 h. The reaction mixture was diluted with $H_2O$ and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with a saturated solution of $NaHCO_3$ and $H_2O$, and dried over $Na_2SO_4$. The solvent was removed under reduced pressure to give residue (24 mg), which was chromatographed on $SiO_2$. Elution with $CHCl_3$–MeOH (15 : 1) gave diol lactone **18** (17 mg), colorless powder, IR ($CHCl_3$), 3500, 1770 $cm^{-1}$; $^1H$ NMR $\delta$ 0.84 (3H, d, $J$=7.5 Hz, 1-$CH_3$), 0.80, 0.91 (3H each, s, 4-$CH_3$, 8-$CH_3$), 1.07 (3H, d, $J$=7.5 Hz, 5-$CH_3$), 2.67 (1H, q, $J$=7.5 Hz, 5-H), 4.13 (1H, d, $J$=2.0 Hz, 9-H) and 5.62 (1H, d, $J$=2.0 Hz, 10-H); MS *m/z* (%) 268 (trace, $M^+$, $C_{15}H_{24}O_4$), 250 [4, $(M-H_2O)^+$], 193 (100), 165 (98), 109 (97), 55 (32).

*Reduction of Ptychanolide* (**4**) *with Lithium Aluminium Hydride*. A solution of ptychanolide **4** (75 mg) in dry ether (2 ml) was added to an ice-cooled solution of LAH (100 mg) in dry ether (4 ml). After addition, the reaction mixture was stirred at room temperature for 2 h followed by the usual work-up afforded a residue. The residue was chromatographed on $SiO_2$ using $CHCl_3$–MeOH (15 : 1) to give triol **19** (75 mg). recrystallization of triol **19** from MeOH yielded colorless plates, mp 118—119 °C, $[\alpha]_D^{28}$ −40.0° (*c* 1.04, $CHCl_3$); IR ($CHCl_3$) 3420, 3250 $cm^{-1}$; $^1H$ NMR $\delta$ 0.69, 0.82 (3H each, s, 4-$CH_3$, 8-$CH_3$), 0.81 (3H, d, $J$=7.7 Hz, 1-$CH_3$), 1.16 (3H, d, $J$=7.7 Hz, 5-$CH_3$), 1.10 (1H, d, $J$=13.6 Hz, 7-$H_A$), 1.42 (1H, d, $J$=13.6 Hz, 7-$H_B$), 2.15 (1H, q, $J$=7.7 Hz, 5-H), 2.65, 3.20 (1H each, m, OH), 3.26 (1H, br.s, OH), 3.64, 3.84 (1H each, AB type, $J$=14.4 Hz, $-C\underline{H}_2OH$), 3.72 (1H, dd, $J$= 7.2, 14.4 Hz, $-CH-HC\underline{H}-OH$), 3.76 (1H, dd, $J$=4.0, 14.4 Hz, $-CH-HC\underline{H}-OH$) and 3.92 (1H, dd, $J$=4.0, 7.2 Hz, $-C\underline{H}(OH)-CH_2OH$); MS *m/z* (%) 225 [75, $(M-31)^+$], 207 (80), 189 (58), 109 (100). Found: C, 69.98; H, 11.04%. Calcd for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01%.

*Oxidation of Triol* **19** *with* $NaIO_4$. A solution of $NaIO_4$ (25 mg) in $H_2O$ (1 ml) was added to a solution of triol **19** (20 mg) in MeOH (1 ml) and the mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with $H_2O$ and extracted with ether. The residue after usual treatment was chromatographed on $SiO_2$ and elution with $CHCl_3$–MeOH (25 : 1) afforded aldehyde **20** (16 mg), colorless oil, $[\alpha]_D^{25}$ −3.3° (*c* 0.42, $CHCl_3$); IR (film) 3560, 3450, 1715 $cm^{-1}$; $^1H$ NMR $\delta$ 0.81 (6H, s, 4-$CH_3$, 8-$CH_3$), 0.89 (3H, d, $J$=7.5 Hz, 1-$CH_3$), 0.92 (3H, d, $J$=7.5 Hz, 5-$CH_3$), 3.55, 3.94 (1H each, d, $J$=11.0 Hz, $C\underline{H}_2OH$) and 9.69 (1H, s, CHO); MS *m/z* (%) 224 (2, $M^+$), 206 [15, $(M-H_2O)^+$], 195 (51), 181 (100), 109 (90). Found: *m/z* 224.1771. Calcd for $C_{14}H_{24}O_2$: M, 224.1768.

*Oxidation of Aldehyde* (**20**) *with MCPBA*. A solution of aldehyde **20** (16 mg) in $CH_2Cl_2$ (1 ml) was added to a solution of MCPBA (20 mg) and the mixture stirred at room temperature for a day. Then the reaction mixture was treated with $Al_2O_3$ for 30 min. $Al_2O_3$ was removed by filtration and the solvent was evaporated to give a residue, which was purified by column chromatography on $SiO_2$. Elution with $CHCl_3$–MeOH (15 : 1) gave diol **21** (12 mg), colorless oil, $[\alpha]_D^{23}$ −18.4° (*c* 0.57, $CHCl_3$); IR (film) 3325, 1050 $cm^{-1}$; $^1H$ NMR $\delta$ 0.88 (3H, d, $J$=7.5 Hz, 1-$CH_3$), 0.89, 0.93 (3H each, s, 4-$CH_3$, 8-$CH_3$), 0.90 (3H, d, $J$=7.5 Hz, 5-$CH_3$), 1.47 (1H, d, $J$= 13.5 Hz, 7-$H_A$), 1.92 (1H, d, $J$=13.5 Hz, 7-$H_B$), 3.42 (2H, AB q, $J$=11.0 Hz, $-C\underline{H}_2OH$); MS *m/z* (%) 212 (3, $M^+$, $C_{13}H_{24}O_2$), 194 [5, $(M-H_2O)^+$], 181 [100, $(M-31)^+$], 163 (62), 137 (53), 109 (97).

*Oxidation of Diol* **21** *with* $NaIO_4$. A solution of $NaIO_4$ (20 mg) in $H_2O$ (1 ml) was added to a MeOH (1.5 ml) solution of diol **21** (17 mg) and the mixture was stirred at room temperature for a day. The reaction mixture was diluted with $H_2O$ and extracted with hexane. The solvent was removed under vacuum to give a residue (15 mg), which was chromatographed on $SiO_2$. Elution with $CH_2Cl_2$ yielded ketone **22** (9 mg), colorless oil, CD, $\Delta\varepsilon_{295}$ +2.6 (*c* 0.0115, MeOH); IR (film) 1740 $cm^{-1}$; $^1H$ NMR $\delta$ 0.81, 0.87 (3H each, s, 4-$CH_3$, 8-$CH_3$), 0.93, 0.95 (3H each, d, $J$=7.5 Hz, 1-$CH_3$, 5-$CH_3$), 1.55 (1H, d, $J$=13.5 Hz, 7-$H_A$), 2.32 (1H, d, $J$=13.5 Hz, 7-$H_B$) and 2.27 (1H, q, $J$=7.5 Hz, 5-H); MS *m/z* (%) 180 (82, $M^+$, $C_{12}H_{20}O$), 165 [33, $(M-CH_3)^+$], 123 (46), 109 (100), 82 (88).

*Reduction of Ketone* **22** *with Lithium Aluminium Hydride*. A mixture of ketone **22** (9 mg) and LAH (20 mg) in dry ether (3 ml) was stirred at room temperature for 2 h. The reaction mixture was treated in the usual way to give a residue (9 mg), which was purified by column chromatography on $SiO_2$. Elution with $CHCl_3$ gave a minor alcohol **24** (2 mg), colorless oil, IR (film) 3430 $cm^{-1}$; $^1H$ NMR $\delta$ 0.84, 0.90 (3H each, s, 4-$CH_3$, 8-$CH_3$), 0.84 (3H, d, $J$=7.7 Hz, 1-$CH_3$), 0.91 (3H, d,

$J$=7.7 Hz, 5-$CH_3$), 1.42 (1H, dd, $J$=5.4, 13.6 Hz, 7-$H_A$), 1.95 (1H, dd, $J$=7.2, 13.6 Hz, 7-$H_B$), 1.77 (1H, m, 1-H), 1.87 (1H, dq, $J$=7.2, 7.7 Hz, 5-H) and 4.20 (1H, dt, $J$=5.4, 7.2 Hz, 6-H). Successive elution with the same solvent gave a major alcohol **23** (5 mg), colorless oil, IR (film) 3450 $cm^{-1}$; $^1H$ NMR $\delta$ 0.75 (6H, s, 4-$CH_3$, 8-$CH_3$), 0.84 (3H, d, $J$=7.7 Hz, 1-$CH_3$), 0.91 (3H, d, $J$=7.7 Hz, 5-$CH_3$), 1.49 (1H, dd, $J$=7.7, 13.6 Hz, 7-$H_A$), 1.74 (1H, dq, $J$=9.4, 7.7 Hz, 5-H), 1.79 (1H, dd, $J$=7.7, 13.6 Hz, 7-$H_B$), 2.01 (1H, tq, $J$=7.2, 8.1 Hz, 1-H), 3.77 (1H, dt, $J$=9.4, 7.7 Hz, 6-H); MS $m/z$ (%) 164 [32, $(M-H_2O)^+$], 149 [100, $(M-18-15)^+$].

*Conversion of Ketone **22** into Hydrocarbon **25**.* A mixture of ketone **22** (10 mg) in 1,2-ethanedithiol (0.1 ml) and $BF_3$–$Et_2O$ (2 drops) was kept at room temperature for 2 h. The reaction mixture was poured into ice-water, and extracted with ether. The ether layer was washed with a saturated solution of $NaHCO_3$ and $H_2O$, and dried over $Na_2SO_4$. The solvent was removed under vacuum to give a residue, which was desulfurized with Raney Ni (W-4, 50 mg) in EtOH (1.5 ml) under reflux for 2 h. The reaction mixture was filtered and the filtrate was diluted with $H_2O$, and extracted with pentane. The solvent was removed with $N_2$ gas to give a colorless residue, which was subjected to GC separation to yield hydrocarbon **25** (4 mg), colorless oil, $^1H$ NMR $\delta$ 0.73 (6H, s, 4-$CH_3$, 8-$CH_3$), 0.83 (6H, d, $J$=7.7 Hz, 1-$CH_3$, 5-$CH_3$), 1.27 (2H, m, 3-$H_A$, 7-$H_A$), 1.30 (2H, m, 2-$H_A$, 6-$H_A$), 1.50 (2H, m, 3-$H_B$, 7-$H_B$), 1.73 (2H, m, 2-$H_B$, 6-$H_B$), and 1.85 (2H, m, 1-H, 5-H); $^{13}C$ NMR $\delta$ 15.0, 18.0, 31.7, 37.5, 44.4, 53.7; MS $m/z$ (%) 166 (9, $M^+$, $C_{12}H_{22}$), 151 [51, $(M-CH_3)^+$], 109 (61), 84 (100).

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