Terpendoles, Novel ACAT Inhibitors Produced by *Albophoma yamanashiensis*

II. Structure Elucidation of Terpendoles A, B, C and D

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Structures of terpendoles A, B, C and D, novel acyl-CoA: cholesterol acyltransferase (ACAT) inhibitors, were determined by spectroscopic studies. All terpendoles consist of diterpene and indole moieties in common. Terpendoles A, C and D possess an additional isoprenyl unit *via* oxygen atom(s) of their diterpene moieties. The relative stereochemistries of terpendoles C and D were confirmed by NOE experiments and X-ray crystallographic analysis.

Terpendoles produced by *Albophoma yamanashiensis* showed potent inhibitory activity against acyl-CoA: cholesterol acyltransferase (ACAT). Two known related compounds, paspaline[1] and emindole SB[2,3], were also isolated from the culture broth of the producer. The fermentation, isolation, and biological properties of terpendoles have been described in the preceeding paper[4]. We will report herein the structure elucidation of terpendoles A, B, C and D.

Results

Physico-chemical Properties of Terpendoles A, B, C and D

Physico-chemical properties of terpendoles A, B, C and D are summarized in Table 1. The molecular formulas were determined to be $C_{32}H_{41}NO_6$ for A, $C_{27}H_{35}NO_3$ for B, $C_{32}H_{41}NO_5$ for C and $C_{32}H_{43}NO_4$ for D by high resolution electron impact mass spectra (HREI-MS) and fast atom bombardment mass spectra (FAB-MS). Terpendoles showed the same absorption maxima at 225 and 275 nm in the UV spectra, suggesting the presence of indole moiety in their structures. The IR spectra suggested the presence of –OH and/or –NH (3450 cm^{-1}).

Structure of Terpendole C

The ^1H and ^{13}C NMR spectra (Figs. 1 and 2, respectively) of terpendole C showed 41 protons and 32 carbons, supporting the molecular formula. The carbon signals were classified into the following types in the DEPT spectra: $6\times CH_3-$, $5\times -CH_2-$, $1\times >CH-$, $5\times >CH-O-$, $2\times -\overset{|}{\underset{|}{C}}-$, $3\times -\overset{|}{\underset{|}{C}}-O-$, $5\times -CH=$ and $5\times >C=$.

Table 1. Physico-chemical properties of terpendoles A, B, C and D.

	Terpendole A	Terpendole B	Terpendole C	Terpendole D
Appearence	White powder	White powder	White powder	White powder
Molecular weight	535	421	519	505
Molecular formula	$C_{32}H_{41}NO_6$	$C_{27}H_{35}NO_3$	$C_{32}H_{41}NO_5$	$C_{32}H_{43}NO_4$
FAB-MS				
Positive	536 $[M+H]^+$	422 $[M+H]^+$	520 $[M+H]^+$	506 $[M+H]^+$
	558 $[M+Na]^+$	444 $[M+Na]^+$	542 $[M+Na]^+$	528 $[M+Na]^+$
EI-MS	535 $[M]^+$	421 $[M]^+$	519 $[M]^+$	505 $[M+H]^+$
	130, 83	130	130	130, 69
HREI-MS (*m/z*)				
Calcd	535.2934 (for $C_{32}H_{41}NO_6$)	421.2613 (for $C_{27}H_{35}NO_3$)	519.3003 (for $C_{32}H_{41}NO_5$)	505.3197 (for $C_{32}H_{43}NO_4$)
Found	535.2932	421.2615	519.2982	505.3190
$[\alpha]_D^{28}$ (*c* 1.0, CH_3OH)	+11.6°	−3.6°	−2.3°	−31.2°
UV $\lambda_{max}^{CH_3OH}$ (nm)	225, 275	225, 275	225, 275	225, 275
IR ν_{max}^{KBr} (cm^{-1})	3450, 2900, 920	3450, 2900, 920	3450, 2900, 920	3450, 2900, 920

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Fig. 1. ^{1}H NMR spectrum of terpendole C (400 MHz, DMSO-d_6).

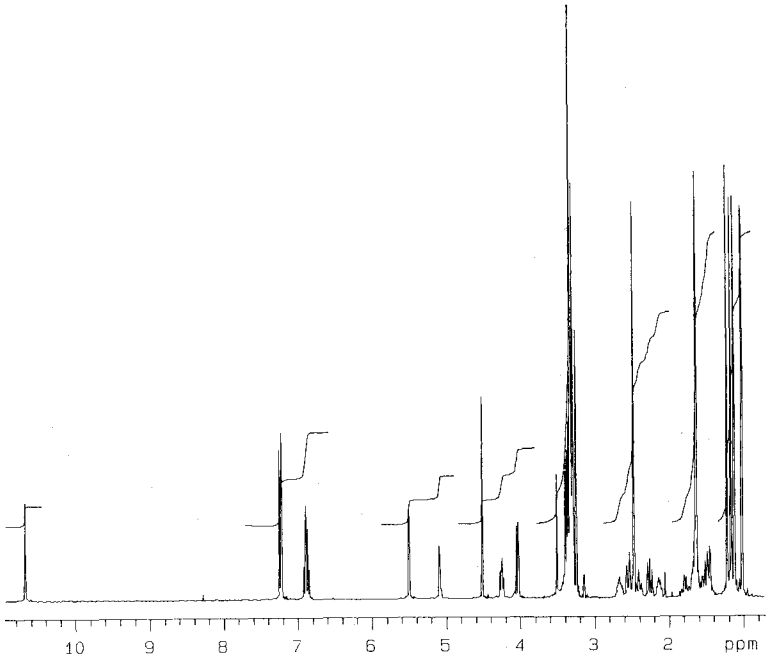
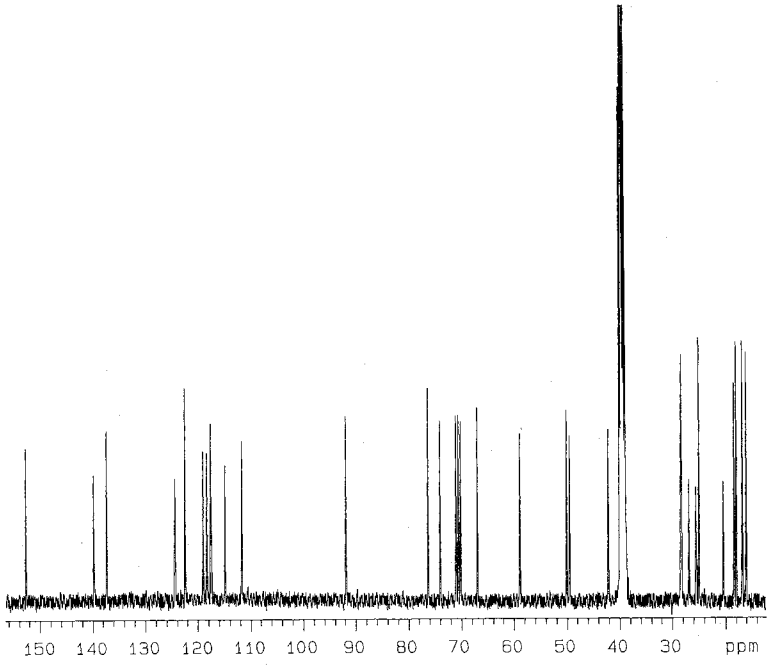


Fig. 2. ^{13}C NMR spectrum of terpendole C (100 MHz, DMSO-d_6).



The connectivity of proton and carbon atoms was assigned by the HMQC spectrum as shown in Table 2.

From the ^{1}H-^{1}H COSY spectrum (Fig. 3), four proton sequences, $-C^{5}H_2-C^{6}H_2-C^{7}H-O-$, $-O-C^{9}H-C^{10}H-O-$, $-C^{15}H_2-C^{16}H-C^{17}H_2-$ and $\begin{matrix}-O\\ \\ -O\end{matrix}\!\!>C^{31}H-C^{33}H=$, were determined. A doublet-like signal at δ 7.24 (H-20 and H-23) coupled with two triplet-like methines (δ 6.87, H-21 and δ 6.91, H-22) in ^{1}H-^{1}H COSY and the long-range couplings were observed from H-21 to C-19 (δ 124.5) and C-23 (δ 111.8) and from H-22 to C-20 (δ 117.6) and C-24 (δ 139.8) in the HMBC spectrum. Therefore, *ortho*-disubstituted benzene was suggested. The long-range couplings from NH-1 (δ 10.69) to C-2 (δ 152.7), C-18 (δ 114.9), C-19 and C-24 and from H-20 to C-18 showed that a pyrrole ring was attached to the benzene, and thus the presence of an indole moiety was confirmed. UV maxima at 225 and 275 nm and a fragment ion peak (m/z 130) of EI-MS supported the presence of the indole moiety. The long-range couplings from H-25

Table 2. ^{1}H and ^{13}C NMR chemical shifts of terpendoles A, B, C and D.

Carbon No.	Terpendole A			Terpendole B			Terpendole C		
	^{13}C chemical shifts (ppm)[a]		^{1}H chemical shifts (ppm)[b]	^{13}C chemical shifts (ppm)[a]		^{1}H chemical shifts (ppm)[b]	^{13}C chemical shifts (ppm)[c]		^{1}H chemical shifts (ppm)[d]
NH-1									10.69 (1H, s)
C-2	152.3			151.8			152.7		
C-3	54.0			51.8			50.2		
C-4	44.0			41.0			42.2		
C-5	27.6	Ha	2.56 (1H, dd, J=13.5, 5.5 Hz)	33.0		1.87 (2H, m)	25.6	Ha	2.41 (1H, m)
		Hb	1.64 (1H, m)					Hb	1.69 (1H, m)
C-6	29.9	Ha	2.20 (1H, m)	30.9	Ha	2.25 (1H, m)	28.5	Ha	2.14 (1H, m)
		Hb	1.77 (1H, m)		Hb	1.88 (1H, m)		Hb	1.64 (1H, m)
C-7	73.4		4.31 (1H, t, J=9.0 Hz)	75.4		3.87 (1H, brt, J=9.0 Hz)	70.7		4.26 (1H, brt, J=9.0 Hz)
C-9	72.9		3.56 (1H, d, J=9.0 Hz)	76.5		3.53 (1H, dd, J=11.0, 2.0 Hz)	71.1		3.39 (1H, d, J=9.5 Hz)
C-10	72.8		3.93 (1H, d, J=9.0 Hz)	27.6	Ha	1.76 (1H, dd, J=14.0, 11.0 Hz)	70.2		4.05 (1H, brd, J=9.5 Hz)
					Hb	2.07 (1H, brt, J=14.0 Hz)			
C-10-OH									
C-11	61.3		3.52 (1H, s)	57.5		3.46 (1H, s)	59.0		3.51 (1H, s)
C-12	69.1			63.4			67.1		
C-13	79.0			42.8		2.08 (1H, s)	76.5		
C-13-OH									4.52 (1H, s)
C-14	30.8	Ha	1.58 (1H, m)	23.4	Ha	1.62 (1H, m)	28.4	Ha	1.53 (1H, m)
		Hb	1.36 (1H, m)		Hb	1.10 (1H, m)		Hb	1.47 (1H, m)
C-15	22.2	Ha	1.91 (1H, brd, J=13.0 Hz)	25.7	Ha	1.70 (1H, m)	20.5	Ha	1.79 (1H, m)
		Hb	1.55 (1H, brd, J=13.0 Hz)		Hb	1.60 (1H, m)		Hb	1.47 (1H, m)
C-16	51.7		2.74 (1H, m)	51.3		2.74 (1H, m)	49.6		2.68 (1H, m)
C-17	28.4	Ha	2.33 (1H, dd, J=13.0, 11.0 Hz)	28.4	Ha	2.34 (1H, dd, J=13.0, 11.0 Hz)	26.9	Ha	2.26 (1H, dd, J=13.0, 10.8 Hz)
		Hb	2.64 (1H, dd, J=13.0, 6.5 Hz)		Hb	2.64 (1H, dd, J=13.0, 6.5 Hz)		Hb	2.56 (1H, dd, J=13.0, 6.2 Hz)
C-18	117.5			118.3			114.9		
C-19	126.8			126.5			124.5		
C-20	119.1		7.29 (1H, m)	119.1		7.28 (1H, m)	117.6		7.24 (1H, m)
C-21	120.0		6.92 (1H, m)	120.0		6.93 (1H, m)	118.4		6.87 (1H, m)
C-22	121.0		6.93 (1H, m)	121.1		6.93 (1H, m)	119.2		6.91 (1H, m)
C-23	112.9		7.28 (1H, m)	112.9		7.28 (1H, m)	111.8		7.24 (1H, m)
C-24	142.1			142.3			139.8		
C-25	19.7		1.30 (3H, s)	15.1		1.02 (3H, s)	16.1		1.17 (3H, s)
C-26	19.3		1.05 (3H, s)	16.8		1.09 (3H, s)	18.0		1.02 (3H, s)
C-27	76.6			72.8			74.1		
C-28	16.8		1.25 (3H, s)	25.9		1.13 (3H, s)	16.7		1.22 (3H, s)
C-29	28.9		1.24 (3H, s)	25.7		1.14 (3H, s)	28.3		1.12 (3H, s)
C-31	96.9		4.70 (1H, d, J=6.3 Hz)				92.0		5.51 (1H, d, J=6.5 Hz)
C-33	64.7		2.79 (1H, d, J=6.3 Hz)				122.5		5.09 (1H, brd, J=6.5 Hz)
C-34	59.3						137.5		
C-35	17.2		1.22 (3H, s)				18.4		1.63 (3H, d, J=1.2 Hz)
C-36	25.0		1.29 (3H, s)				25.1		1.65 (3H, d, J=1.2 Hz)

Carbon No.	Terpendole C			Terpendole D		
	^{13}C chemical shifts (ppm)[e]		^{1}H chemical shifts (ppm)[f]	^{13}C chemical shifts (ppm)[e]		^{1}H chemical shifts (ppm)[f]
NH-1			7.79 (1H, s)			7.85 (1H, s)
C-2	151.7			149.9		
C-3	50.7			50.3		
C-4	42.4			39.5		
C-5	27.4	Ha	2.72 (1H, m)	32.5	Ha	1.90 (1H, dd, J=14.0, 4.0 Hz)
		Hb	1.35 (1H, m)		Hb	1.58 (1H, m)
C-6	28.0	Ha	2.30 (1H, m)	28.9	Ha	2.19 (1H, m)
		Hb	1.80 (1H, m)		Hb	1.72 (1H, m)
C-7	71.5		4.35 (1H, t, J=9.0 Hz)	72.5		3.86 (1H, dd, J=10.0, 7.5 Hz)
C-9	71.1		3.60 (1H, d, J=9.5 Hz)	74.6		3.58 (1H, d, J=9.0 Hz)
C-10	71.2		3.94 (1H, d, J=9.5 Hz)	67.5		4.00 (1H, d, J=9.0 Hz)
C-10-OH						4.70 (1H, s)
C-11	61.1		3.63 (1H, s)	59.4		3.49 (1H, s)
C-12	67.8			64.9		
C-13	78.1			40.6		2.13 (1H, dd, J=12.5, 3.0 Hz)
C-13-OH			—[g]			
C-14	30.3	Ha	1.60 (1H, m)	22.0	Ha	1.71 (1H, m)
		Hb	1.44 (1H, m)		Hb	1.07 (1H, m)
C-15	20.6	Ha	1.94 (1H, m)	24.1	Ha	1.72 (1H, m)
		Hb	1.65 (1H, m)		Hb	1.57 (1H, m)
C-16	50.0		2.80 (1H, m)	49.5		2.78 (1H, m)
C-17	27.2	Ha	2.43 (1H, dd, J=13.0, 10.5 Hz)	27.2	Ha	2.37 (1H, dd, J=13.0, 10.0 Hz)
		Hb	2.74 (1H, dd, J=13.0, 6.5 Hz)		Hb	2.70 (1H, dd, J=13.0, 6.5 Hz)
C-18	117.6			118.4		
C-19	125.1			125.0		
C-20	118.5		7.45 (1H, m)	118.5		7.44 (1H, m)
C-21	119.6		6.09 (1H, m)	119.6		7.09 (1H, m)
C-22	120.5		6.09 (1H, m)	120.5		7.09 (1H, m)
C-23	111.4		7.32 (1H, m)	111.5		7.31 (1H, m)
C-24	139.7			137.2		
C-25	16.0		1.28 (3H, s)	14.5		1.00 (3H, s)
C-26	16.6		1.08 (3H, s)	16.2		1.08 (3H, s)
C-27	74.7			79.1		
C-28	18.8		1.14 (3H, s)	19.2		1.24 (3H, s)
C-29	28.3		1.32 (3H, s)	23.5		1.29 (3H, s)
C-31	92.6		5.56 (1H, d, J=6.5 Hz)	58.0		3.96 (2H, brd, J=7.0 Hz)
C-33	122.0		5.33 (1H, d, J=6.5 Hz)	120.6		5.26 (1H, brt, J=6.5 Hz)
C-34	139.6			139.9		
C-35	18.6		1.75 (3H, s)	17.9		1.66 (3H, s)
C-36	25.7		1.75 (3H, s)	25.7		1.71 (3H, s)

[a] Chemical shifts are shown with reference to CD_3OD as 49.8 ppm. [b] Chemical shifts are shown with reference to CD_3OD as 3.30 ppm. [c] Chemical shifts are shown with reference to DMSO-d_6 as 39.5 ppm. [d] Chemical shifts are shown with reference to DMSO-d_6 as 2.48 ppm. [e] Chemical shifts are shown with reference to $CDCl_3$ as 77.7 ppm. [f] Chemical shifts are shown with reference to $CDCl_3$ as 7.26 ppm. [g] Not detected.

Fig. 3. ^{1}H-^{1}H COSY, HMBC and ^{13}C-^{1}H long-range COSY experiments of terpendole C.

▬: ^{1}H-^{1}H couplings obtained from ^{1}H-^{1}H COSY, ⟶: long-range couplings obtained from HMBC and ^{13}C-^{1}H long-range COSY experiments.

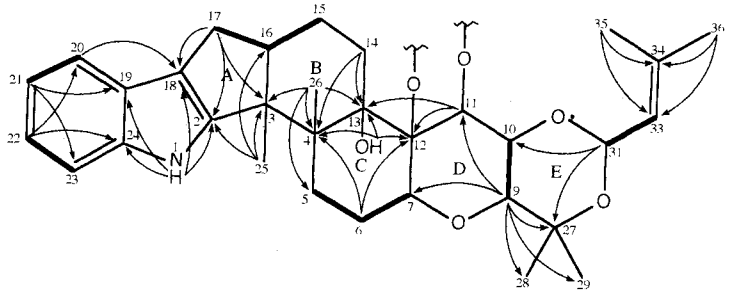


Fig. 4. NOE experiments of terpendole C (⟶: NOEs obtained from differential ^{1}H decoupling NOE experiments).

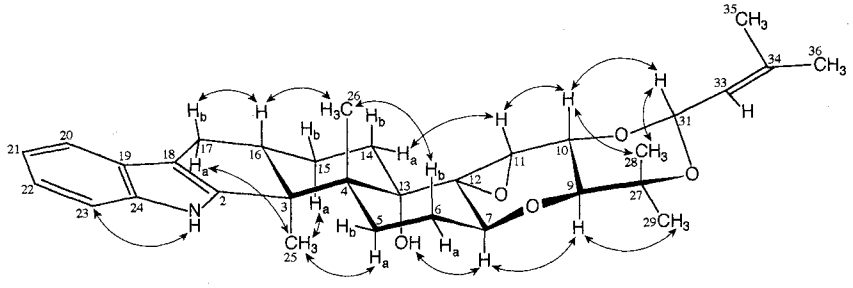
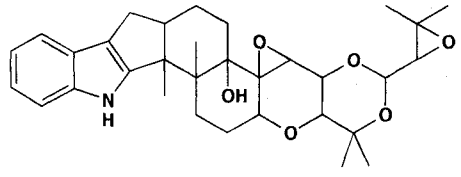
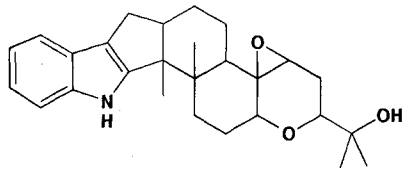


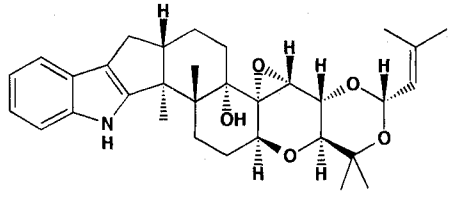
Fig. 5. Structures of terpendoles A, B, C and D.



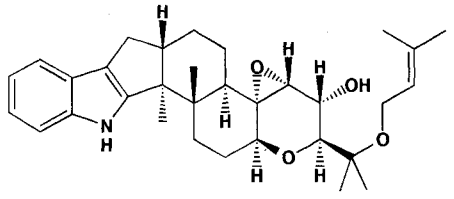
Terpendole A



Terpendole B



Terpendole C



Terpendole D

(δ 1.17) to C-2, C-3 (δ 50.2) and C-16 (δ 49.6) and from H_2-17 (δ 2.26, 2.56) to C-2, C-3 and C-18 suggested the cyclopentane ring (ring A) attached to the indole moiety. The long-range couplings were observed from H-26 (δ 1.02) to C-3, C-4 (δ 42.2), C-5 (δ 25.6) and C-13 (δ 76.5), from H_2-14 (δ 1.47, 1.53) to C-4 and C-13, from 13-OH (δ 4.52) to C-4, C-12 (δ 67.1) and C-13, and from H_2-6 (δ 1.64, 2.14) to C-4 and C-12. The signals of H_2-14 and H_2-15 (δ 1.47, 1.79) were overlapped in the spectrum taken in DMSO-d_6, but they were clearly separated in $CDCl_3$ (H_2-14, δ 1.44, 1.60; H_2-15, δ 1.65, 1.94) and the couplings were observed between them in ^{1}H-^{1}H COSY. These data revealed the presence of two cyclohexane rings (rings B and C). The presence of tetrahydropyrane (ring D) and 1,3-dioxane rings was shown by the long-range couplings observed from H-11 (δ 3.51) to C-12 and C-13, from H-9 (δ 3.39) to C-7 (δ 70.7), C-11 (δ 59.0), C-27 (δ 74.1), C-28 (δ 16.7) and C-29 (δ 28.3), and from H-31 (δ 5.51) to C-10 (δ 70.2) and C-27. The long-range couplings from H_3-35 (δ 1.63) and H_3-36 (δ 1.65) to C-33 (δ 122.5) and C-34 (δ 137.5) suggested an isobutenyl residue connected to the ring E.

From these spectroscopic data, the structure of terpendole C was deduced except for the substituents at C-11 and C-12. Taking the molecular formula in consideration, the remaining atom is one oxygen, suggesting epoxide formation between C-11 and C-12.

The configuration of terpendole C was examined by the NOESY experiment. As shown in Fig. 4, the NOEs from H_3-25 to H_a-5 (δ 2.41), H_a-15 (δ 1.69) and H_a-17 (δ 2.26) showed that the methyl group C-25 was axial. In the same manner, the NOEs between H-7 (δ 4.26) and H-9, H-7 and 13-OH, H_b-6 (δ 1.64) and H_3-26, and H-16 (δ 2.68) and H_3-26 suggested that they were all axial. The NOEs among H-10 (δ 4.05), H_3-28 (δ 1.22) and H-31 showed that they are also axial. The oxymethine proton of H-11 was suggested to be equatorial since the NOE was observed between H-10 and H-11. From the results described above, the relative configuration of terpendole C is shown in Fig. 5.

Structure of Terpendole D

The ^{13}C NMR spectra of terpendole D was similar to those of terpendole C except for the two carbon signals of C-13 and C-31 (Table 2), that is, the methine carbon of C-13 (δ 40.6) and the oxymethylene carbon of C-31 (δ 58.0) for terpendole D. In the ^1H-^1H COSY spectrum, the couplings observed between the methine proton of H-13 (δ 2.13) and the methylene proton of Hb-14 (δ 1.07) suggested the absence of 13-OH in terpendole C. The hemiketal carbon at C-31 in terpendole C was found to be reduced in terpendole D because of 1) the observation of ^1H-^1H couplings between the oxymethylene proton of H_2-31 (δ 3.96) and the sp^2 methine proton of H-33 (δ 5.26) and 2) the fragment ion peak at *m/z* 69 observed in the EI-MS, indicating the presence of an isoprenyl residue. The structure of terpendole D was further confirmed by the HMBC experiments. As shown in Fig. 6, the long range couplings from the hydroxy proton of 10-OH (δ 4.70) to the carbons of C-9 (δ 74.6), C-10 (δ 67.5) and C-11 (δ 59.4) indicated the presence of 10-hydroxy and isoprenyl residues. The NOE experiments of terpendole D suggested the same relative configuration as terpendole C (data not shown).

X-ray Crystallographic Analysis of Terpendole D

In order to confirm the stereostructures deduced by NOE experiments, a single crystal X-ray crystallographic analysis of terpendole D was carried out using the sample obtained by recrystallization from MeOH. The analytical data are summarized in Table 3 and the relative configuration of terpendole D obtained is shown in Fig. 7. The structure was solved by direct methods[5,6] and the non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1119 observed reflections and 334 variable parameters and converged with unweighted and weighted agreement factors of $R=0.065$, $R_W=0.049$.

Fig. 6. ^1H-^1H COSY, HMBC and ^{13}C-^1H long-range COSY experiments of terpendole D (▬: ^1H-^1H couplings obtained from ^1H-^1H COSY, ⟶: long-range couplings obtained from HMBC and ^{13}C-^1H long-range COSY experiments).

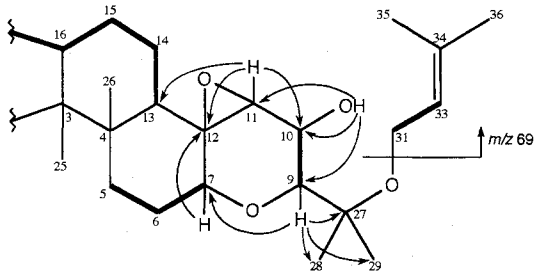
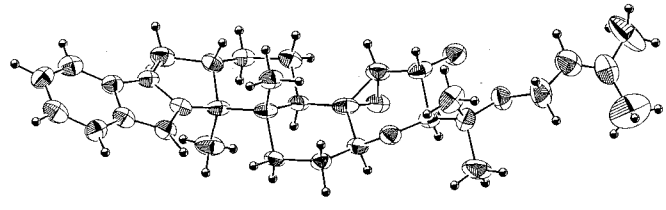


Table 3. Single crystal X-ray crystallographic analysis.

Crystal parameters	
Empirical formula	$C_{32}H_{42}NO_4$
Formula weight	504.69
Crystal dimensions (mm)	$0.2\times0.4\times0.2$
Crystal system	Orthorhombic
Lattice Parameters:	a = 18.957 (5) Å
	b = 21.651 (2) Å
	c = 6.773 (2) Å
	V = 2780 (1) Å^3
Space group	$P2_12_12_1$ with Z = 4
Density calc (g/cm^3)	1.206
Linear absorption factor (cm^{-1})	5.84
Refinement parameters	
No. of reflections measured	3,054
Nonzero reflections ($I>3.00\sigma$)	1,119
R-indexa Residuals: R[a]	0.065
Residuals: R_W[b]	0.049
Goodness of fit indicator[c]	3.17

[a] $\Sigma||F_o|-|F_c||/\Sigma|F_o|$
[b] $[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o)]^{1/2}$
[c] $[\Sigma w(|F_o|^2-|F_c|^2/(No-Nv)]^{1/2}$
No = number of observations
Nv = number of variables

Fig. 7. Relative molecular structure of terpendole D determined by X-ray crystallography.

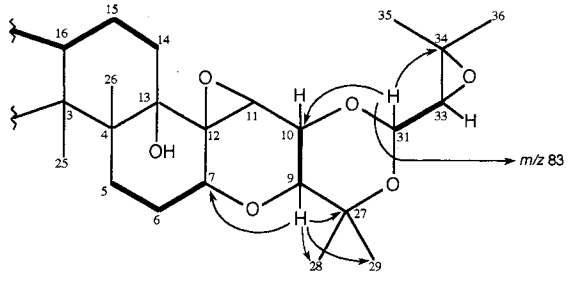


Structures of Terpendoles A and B

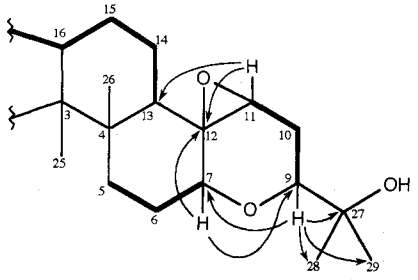
The spectral data of terpendole A obtained from FAB-MS ($C_{32}H_{41}NO_6$) and NMR (Table 2) experi-

Fig. 8. ^{1}H-^{1}H COSY, HMBC and ^{13}C-^{1}H long range COSY experiments of terpendoles A and B.

▬: ^{1}H-^{1}H couplings obtained from ^{1}H-^{1}H COSY, ⟶: long-range couplings obtained from HMBC and ^{13}C-^{1}H long-range COSY experiments.



Terpendole A



Terpendole B

ments suggested its structure as an oxidative compound of terpendole C. The ^{13}C NMR and DEPT spectra of terpendole A were similar to those of terpendole C except for the presence of the C-33 oxymethine (δ 64.7) and C-34 oxyquaternary carbons (δ 59.3) for terpendole A in place of the corresponding olefinic carbons for terpendole C. The assignment of C-33 and C-34 were confirmed by HMQC and HMBC (Fig. 8). These results indicated that terpendole A has an epoxide moiety at the C-33 and C-34 positions. Moreover, the fragment ion at *m/z* 83 indicated the presence of an epoxyprenyl moiety (Fig. 8). Thus the structure of terpendole A was determined as shown in Fig. 5.

Comparison of the spectral data of terpendole B with those of terpendole D revealed that 1) one prenyl moiety (C_5H_9) and one oxygen atom are lacking in terpendole B, and 2) the methylene carbon of C-10 (δ 27.6) was observed in terpendole B instead of oxymethine one (δ 67.5) in terpendole D from the ^{13}C NMR (Table 2) and DEPT spectra. In the ^{1}H-^{1}H COSY spectrum (Fig. 8), the couplings were observed from the methylene protons of H_2-10 (δ 1.76 and 2.07) to the oxymethine protons of H-9 (δ 3.53) and H-11 (δ 3.46), indicating the –O–CH–CH_2–CH–O– sequence. The structure of terpendole B was further confirmed by the HMBC experiments (Fig. 8). The long-range couplings between the oxymethine proton of H-9 and the carbons of C-27 (δ 72.8), C-28 (δ 25.9) and C-29 (δ 25.7), between the oxymethine proton of H-7 (δ 3.87) and the carbons of C-9 (δ 76.5) and C-12 (δ 63.4), and between the oxymethine proton of H-11 and the carbon of C-12 indicated the hydropyrane structure. Taken together, the structure of terpendole B was determined as shown in Fig. 5.

Discussion

Indoloditerpenes consisting of indole and diterpene moieties are proposed to be classified into three groups, namely, nominine, emindole and paspaline groups, on the structural basis[7]. Terpendoles, emindole SB and paspaline, produced by *Albophoma yamanashiensis*, belong to the paspaline group, in which reactions of cyclization and condensation between an indole (derived from tryptophane) and a diterpene (geranylgeraniol) occur to produce emindole SB first, then paspaline. After various reactions including demethylation at the 12-methyl group[8], many compounds of this group are biosynthesized, such as aflatrem[9], paxilline[3,10], paspalicine[1], janthitrems[11,12], lolitrems[13], penitrems[14~16] and terpendoles. The relative stereostructures of terpendoles C and D were confirmed by the NOE experiments and X-ray analysis to show that their stereostructures of the diterpene moieties are the same as lolitrem B. Furthermore, terpendoles A and B appeared to have the same stereostructures as terpendoles C and D due to the similar coupling constants and chemical shifts of their methylene and methine protons.

Experimental

Spectroscopic Studies

^{1}H and ^{13}C NMR spectra were obtained on a Varian XL-400 spectrometer. MS spectra were measured on a JEOL model DX-300 spectrometer. UV and IR spectra were recorded on a Shimadzu model UV-200S spectrophotometer and a Jasco model A-102 infrared spectrophotometer, respectively.

Single Crystal X-Ray Analysis

A colorless plate crystal having approximate dimensions of $0.2 \times 0.4 \times 0.2$ mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC-5R diffractometer with graphite monochromated CuKα radiation. The data were collected at a temperature of 23 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 145.2°. Pertinent crystal, data collection, and refinement parameters are summarized in Table 3. Neutral atom scattering factors were taken from CROMER and WABER[17]. Anomolous dispersion effects were included in Fcalc[18]; the values for $\Delta f'$ and $\Delta f''$ were

those of CROMER[17]. All calculations were performed using the TEXSAN[19] crystallographic software package of Molecular Structure Corporation.

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